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Lead metallic–lead dioxide glasses as alternative of immobilization of the radioactive wastes

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ABSTRACT

In this work, we report structural, optical and electrochemical investigations on the gadolinium–lead glass system with the $xGd_2O_3 \cdot (100 - x)[4PbO_2 \cdot Pb]$ composition where x = 0, 1, 5, 10, 15 mol% Gd_2O_3 obtained by the melt quenching method. The studied homogeneous glass system was characterized by X-ray diffraction (XRD), infrared (IR) spectroscopy, ultraviolet–visible (UV–VIS) spectroscopy, electron paramagnetic resonance (EPR) spectroscopy, and cyclic voltammetry (CV) measurements. The purpose of this paper was i) to immobilize the gadolinium ions in the lead–lead dioxide glasses and ii) to investigate the structural, optical and electrochemical properties of the obtained glasses for possible applications in the radioactive waste recycling.

IR data show that the $[PbO_6]$ octahedral structural units do not accommodate with the excess of non-bridging oxygen, $[PbO_3]$ pyramidal units are suitable neighbors for the gadolinium ions and $[GdO_n]$ entities will be intercalated in the host matrix. The EPR spectra of Gd^{+3} ions in lead–lead dioxide glasses exhibit four resonance lines situated at about $g \approx 2.0$; 2.8; 4.8 and 6. The EPR signals located at about g ~ 2; 2.8 and 6 are known as the U-spectrum of Gd^{+3} ions situated in higher symmetry which can be readily accommodated in a vitreous system whereas the sharpness of the signal situated at about g ~ 4.8 is associated with Gd^{+3} ions having low coordination numbers.

These structural modifications are supported by the increase in the intensity of the UV–VIS absorption bands associated to the electronic transitions of the Pb^{+2} and Gd^{+3} ions and the formation of non-bridging oxygen centers. Electrochemical performances of electrode glasses show the pronounced mobility of the lead ions comparative with the gadolinium ions.

1. Introduction

Immobilization of radioactive wastes by vitrification is a well established process that has been studied extensively over the last 40 years [1–3]. Vitrification has been selected for immobilization of high-level toxic and radioactive wastes because glass is highly stable, very durable and has the ability to incorporate a wide variety of chemical contaminants.

The main advantages of the vitrification route include the fact that glass is a good solvent for wastes, can be processed at reasonably low temperatures, is very tolerant of variations in waste composition, exhibits reasonable chemical durability, is radiation resistant and can accommodate changes of nuclear wastes occurring during decays [4,5].

Various glass systems have been found to be suitable to play the role of a host matrix for nuclear wastes being thermally and mechanically stable and showing good chemical durability. Most current research on vitrification of mixed waste has focused on borosilicate and phosphate glasses, originally developed for immobilization of high-level radioactive waste (HLW). Such borosilicate glasses demonstrated good long-term chemical durability and good thermal and physical stability, but require relatively high temperature processes (1050–1250 °C) for effective encapsulation of wastes [1]. These high temperatures are a major drawback because volatilization of certain isotopes (^{99}Tc and ^{137}Cs) and heavy metals (Pb and Cd) can occur, requiring the use of supplementary procedures to capture and stabilize these off-gas contaminants.

The phosphate glass systems have a low melting point but have little commercial applicability due to their rapid degradation in water and poor chemical durability [6–9]. Thus, borosilicate glasses were found to be, overall, more favorable for the immobilization of HLW.

The future is directed towards the identification of similar glasses with improved durability and processing characteristics, which will mainly be achieved through compositional modifications of existing waste forms [10]. Then, other types of glass waste form with lower manufacturing temperature and easier processing route also offers potential directions for the further studies.

Oxide glasses based on PbO_2 are of great interest because they can form amorphous materials without traditional network formers like SiO_2. The lead dioxide is known as a non-conventional network former.

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Due to its properties like low melting point, corrosion resistant and radiation resistant, lead is indispensable in the radioactive wastes. On the other hand, lead plays a very important role in glasses due to its ability to form both covalent and ionic bonds with oxygen ions from the host matrix [11–15].

In this respect, this work proposes the study of oxidic vitreous systems of lead dioxide–lead metallic doped with gadolinium(III) oxide. The use of the rare earth ions as dopants presents the advantage of the study of the behavior of some ions whose electronic pattern is very similar to that of actinide ions but is not radioactive, thus simplifying the conditions of the research work. Such dopant ions are used in order to "imitate" the behavior of uranium or plutonium ions that represents an important segment of the nuclear wastes.

The aim of the present paper is i) to obtain lead based glasses, that contain metallic lead and lead dioxide, at low temperature due to the lead volatility and ii) to immobilize the gadolinium ions in the lead–lead dioxide glasses for potential applications in the recycling engineering and radioactive waste management. The novelty is given not only by the cheap synthesis method proposed, namely the melt quenching method which is very unusual in materials science for a glass formed only from lead, but also by the immobilized gadolinium ions in the host matrix glasses.

Lead dioxide occurs in an orthorhombic α-phase, a tetragonal β-phase, and a high-pressure γ-phase cubic modification [16,17]. In the structure of the α- and β-PbO_2 modification, each lead atom is surrounded by a distorted octahedron of six oxygen atoms. The β-PbO_2 phase as a representative of a rutile type consists of columns of edge-sharing [PbO_6] octahedral units along the z-axis. Each octahedron of such a chain shares two edges with two neighboring octahedral. These columns of occupied octahedral units alternate with similar columns of empty octahedral units in directions x and y to form a framework. The α-PbO_2 phase consists of zig-zag chains of [PbO_6] octahedral units in the z direction, and each octahedron shares two edges with other octahedral in the chain. The octahedron in α-PbO_2 phase is very irregular and the Pb1 and Pb3 atoms are connected by translation.

Recent experiments and theoretical calculations show that group-IV element dioxide SiO_2, GeO_2, SnO_2 and PbO_2 have a common sequence of high-pressure structural transformations: rutile-type → $CaCl_2$-type → α-PbO_2-type [18]. For example, the β-PbO_2 → α-PbO_2 phase transition occurs at about 590 °C and 1.8 atm [17]. A study of glass formation in this system should therefore be very interesting.

Glass system with the $xGd_2O_3 \cdot (100 - x)[4PbO_2 \cdot Pb]$ composition, where $x = 0 \div 15\%$ Gd_2O_3, was prepared by the classical melt quenching technique and was characterized by XRD, FTIR, UV–VIS and EPR spectroscopies and cyclic voltammetry. Moreover, this study is extended in order to study the effect of Gd_2O_3 concentration on structural, optical, and electrochemical properties and to justify the induced modifications and the status of gadolinium ions in the lead–lead dioxide host glass.

2. Materials and method

Host glass was prepared using reagent grade purity lead (IV) oxide and metallic oxide of high purity in suitable proportion. The mechanically homogenized mixtures were melted in sintered corundum crucibles at 950 °C in an electric furnace. The samples were put directly into the electric furnace at this temperature. After 10 min, the molten material was quenched at room temperature by pouring onto a stainless-steel plate. Appropriate amounts of PbO_2, Pb and Gd_2O_3, having desired stoichiometry, were synthetized by the melt quenching method described before.

The crystalline or amorphous nature of obtained samples (after the transformation of obtained samples into a fine powder) was investigated through the X-ray diffraction method using a XRD-6000 Shimadzu diffractometer, with a graphite monochromator for Cu Kα radiation ($\lambda = 1.54$ Å).

The absorption IR spectra were recorded at room temperature using a JASCO FTIR 6200 spectrometer using the standard KBr pellet disk technique. The spectra were carried out with a standard resolution of 2 cm^{-1}.

Electron paramagnetic resonance measurements were performed at room temperature, in the X frequency band (9.1–9.7 GHz), using an Adani PS 8400-type spectrometer.

Ultraviolet–visible absorption spectra of the powdered glass samples were recorded at room temperature in the 250–600 nm range using a Perkin-Elmer Lambda 45 UV/VIS spectrometer equipped with an integrating sphere. These measurements were made on a glass powder dispersed in KBr pellets. The validity of the band position is ±2 nm.

The electrochemical properties were characterized by cyclic voltammetry using a VERSASTAT3 potentiostat and V3Studio software. Disks of glasses were used as the working electrode, platinum electrode as the counter, calomel as the reference electrode and sulfate acid solution as the liquid electrolyte. All experiments were conducted in an H_2SO_4 solution with a concentration of 5%.

3. Results

The diffraction patterns of glasses with $x = 0$ and 15 mol% Gd_2O_3 shown in Fig. 1 reveal only two large halos specific to amorphous structure. Therefore, the X-ray diffraction patterns did not suggest any crystalline phase in the samples.

The formation of the PbO_2 glassy can be described from the anion-centered perspective of the α-PbO_2 crystal structure. Each oxygen atom is coordinated by three Pb atoms, resulting in an almost regular triangle. The Pb – O bond length variations are insignificant (2.11, 2.17, 2.21 Å) and variations of bond angles are very large (76–100° instead of 90° and 155–171° instead of 180°). Then, the individual Pb – O – Pb angles are different (average value is 118.4°) and depend on temperature [17]. Accordingly, the fact that the average angle is smaller than 120° produces the displacement of the central oxygen atom located beneath the plane of the triangle. These structural modifications imply the decrease of the connectivity of the three-dimensional framework, the apparition of [PbO_3] and [PbO_4] structural units between octahedrons and further the formation of the amorphous structure.

Fig. 2 illustrates the compositional evolution of the FTIR spectra of gadolinium–lead–lead dioxide glasses containing varying Gd_2O_3 concentrations. The infrared bands can be assigned to the [PbO_3], [PbO_4] and [PbO_6] structural units. The band situated at about 460 cm^{-1} visible on the spectra of all series of glasses is assigned to the Pb – O – Pb and

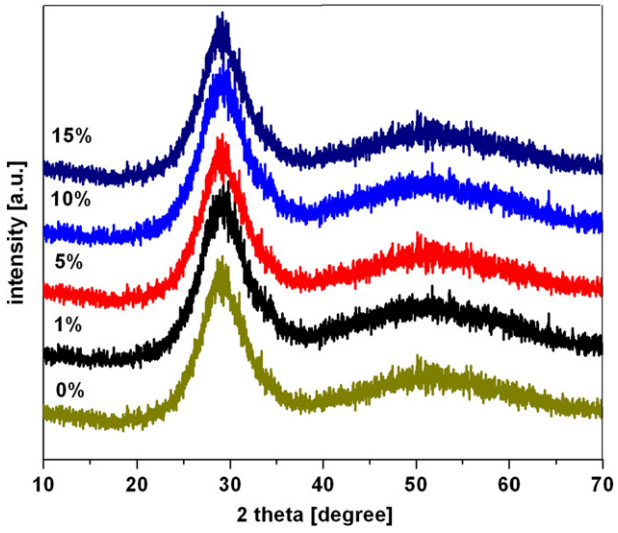

Fig. 1. XRD diffractograms of the $xGd_2O_3 \cdot (100 - x) \cdot [4PbO_2 \cdot Pb]$ glasses with $x = 0$ and 15% Gd_2O_3.